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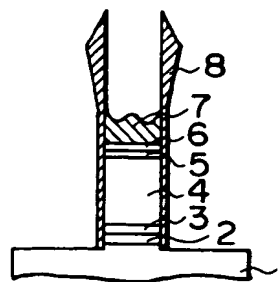
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**Cleaning agent for semiconductor device and method for manufacturing semiconductor device.**

There are disclosed a method of manufacturing a semiconductor device by forming a mask with a photoresist on a conductive layer formed on a semiconductor substrate and then forming a wiring structure by dryetching which method comprises a cleaning step of peeling a protecting deposition film formed on side walls of the conductive layer and the photoresist by using a cleaning agent for a semiconductor device comprising an aqueous solution containing a specific quaternary ammonium salt and a fluoro-compound; and a cleaning agent for a semiconductor device which comprises a specific quaternary ammonium salt and a fluoro-compound, and optionally an organic solvent selected from the group consisting of amides, lactones, nitriles, alcohols and esters. The use of the above cleaning agent in the method of manufacturing a semiconductor device can peel out the protecting deposition film with extreme certainty, whereby the surface of the

conductive layer is decontaminated to high cleanliness and corrosion problem is eliminated.



**FIG. 3**

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## BACKGROUND OF THE INVENTION

### 1. Field of the Invention

The present invention concerns a cleaning agent to be used in a process for manufacturing a semiconductor device and a method of manufacturing a semiconductor device.

### 2. Description of the Related Arts

In the process for manufacturing a semiconductor device, an etching fabrication technology utilizing chemical reaction has been used as a method of forming a wiring structure on a semiconductor substrate by using a conductive material.

Generally, a method of at first applying a mask fabrication technology by photoresist and then removing a non-masked portion by using a chemical or a reactive gas has been conducted. In recent semiconductor industries intending for high integration degree, fabrication for microscopic processing is required. In particular, a fabrication of metal film wirings has been demanded more and more and a fabrication technique aimed for accuracy of within 0.5  $\mu\text{m}$  has been demanded for semiconductor device at present.

In order to attain the purpose, it is demanded to improve the fabrication accuracy of the photoresist and also improve the dryetching technique for removing the non-masked portion. Referring particularly to the photoresist, there are used not only conventional single-layer resist of positive or negative type but also multilayer resist using a combination of such resist and other resin.

Further, in the dryetching technique, anisotropic etching has been advanced with the establishment of a technique for side wall protecting deposition films by using the photoresist and reactive gases, whereby more advanced selective etching has been carried out.

As a disadvantage accompanying the establishment of such techniques, there are mentioned an extreme difficulty in the method of removing the side wall protective deposition films, and corrosion of metal wiring materials. If the side wall protecting deposition film has not been removed sufficiently, radicals or ions in the reaction gas incorporated into the side wall protecting deposition film react with absorbed moisture to form an acid when left in the air after the completion of etching. The resultant acid corrodes wiring materials to bring about a significant adverse effect such as an increase in resistance and wire disconnection. Such a phenomenon frequently occurs, in particular, in aluminum and aluminum alloys used generally as the wiring material.

For preventing such corrosion, there has been adopted a method wherein chlorine radicals or ions are washed away by performing ultrapure-water cleaning for a long period of time after dryetching. However, it is extremely difficult to completely remove chlorine ions or radicals from the side wall protective deposition film by this method, so that a danger of causing corrosion can not completely be eliminated. Accordingly, it is indispensable to completely remove the side wall protecting deposition film in order to thoroughly prevent the corrosion.

For removing such a side wall protecting deposition film, a resist cleaning agent composed of an acidic organic solvent or of an alkaline organic solvent has been used.

As the resist cleaning agent composed of the acidic organic solvent, there is generally used a cleaning agent prepared by adding a phenolic compound, chloro-solvent or an aromatic hydrocarbon to alkylbenzenesulfonic acid. However, the use of this cleaning agent can not completely remove the side wall protecting deposition film even with a heat treatment at a temperature of 100 °C or higher. Further, since the resist cleaning agent composed of the acidic organic solvent is less soluble in water, it is necessary to clean with an organic solvent compatible with water such as isopropanol after the removing operation and then wash with water, which however complicates the process.

On the other hand, it is also considerably difficult to remove the side wall protecting deposition film by using the resist cleaning agent composed of the alkaline organic solvent even by heating to a temperature of 100 °C or higher as is the case with the acidic cleaning solution. As described above, since the side wall protecting deposition film can not completely be removed by using either the acidic or alkaline cleaning agent, the occurrence of corrosion caused by residual chlorine radicals or ions is inevitable.

As a method different from the cleaning method described above, there has been known a method of removing the residual resist after plasma ashing by using an alkaline aqueous solution such as a positive type resist developing solution containing tetramethylammonium hydroxide (Japanese Patent Application Laid-Open No. Sho 62(1987)-281332). In this method, however, a conductive layer made of an aluminum-containing substrate is violently corroded by the alkaline aqueous solution.

Further, for the protecting deposition film formed upon dryetching of a titanium or tungsten layer, a method of removing the film has not yet been established. The titanium or tungsten layer is frequently used as metal wirings for an intermediate layer upon making a conductive layer into a multilayer structure in a semiconductor device.

If the resultant side wall protecting deposition film is left as it is, adjacent wirings are brought into contact with the side wall protecting deposition film, for example, owing to the pressure of the deposition film in the succeeding step to cause short-circuit or abnormality in wirings.

As described above, while various methods have been employed in a production process of a semiconductor device for removing the side wall protecting deposition film formed on the side walls of the conductive layer or photoresist formed on the semiconductor substrate, there are such problems as the occurrence of corrosion. Thus, it has been required to develop a cleaning agent for a semiconductor device capable of easily removing the side wall protecting deposition film and preventing corrosion to the metal conductive layer upon cleaning.

An object of the present invention is to overcome the foregoing problems and provide a cleaning agent for a semiconductor device capable of easily removing a side wall protecting deposition film formed by dryetching, and preventing corrosion to a conductive layer made of various kinds of metallic materials as the wiring material without causing any corrosion at all to any part, as well as a method of manufacturing a semiconductor device capable of manufacturing circuit wirings with high accuracy.

### SUMMARY OF THE INVENTION

As a result of an earnest study for solving the foregoing subject, the present inventors have found that a cleaning agent for a semiconductor comprising an aqueous solution containing a quaternary ammonium salt and a fluoro-compound or an aqueous solution containing a quaternary ammonium salt, a fluoro-compound and an organic solvent selected from the group consisting of amides, lactones, nitriles, alcohols and esters exhibits excellent characteristics including removability for a side wall protecting deposition film formed upon dryetching, corrosion inhibition, non-corrosivity to wiring materials and good workability. The present invention has been accomplished on the basis of the aforesaid finding.

Specifically, the present invention provides a cleaning agent for a semiconductor device which comprises a quaternary ammonium salt represented by the general formula:



in which R represents an alkyl group of 1 to 4 carbon atoms or a hydroxyl-substituted alkyl group of 1 to 4 carbon atoms,  $R_1$  represents an alkyl group of 1 to 4 carbon atoms and X represents an

organic or inorganic acid group; and a fluoro-compound.

The present invention further provide a cleaning agent for a semiconductor device which comprises the above-mentioned quaternary ammonium salt and at least one organic solvent selected from the group consisting of amides, lactones, nitriles, alcohols and esters; and the fluoro-compound.

The present invention still further provides a method of manufacturing a semiconductor device by forming a mask with a photoresist on a conductive layer formed on a semiconductor substrate and containing at least one of titanium, tungsten, aluminum and an aluminum alloy and then forming a wiring structure by dryetching which method comprises a cleaning step of peeling a protecting deposition film formed on side walls of the conductive layer and the photoresist by using a cleaning agent for a semiconductor device comprising a quaternary ammonium salt represented by the general formula:



in which R represents an alkyl group of 1 to 4 carbon atoms or a hydroxyl substituted alkyl group of 1 to 4 carbon atoms,  $R_1$  represents an alkyl group of 1 to 4 carbon atoms and X represents an organic or inorganic acid group; and a fluoro-compound.

### BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is a cross sectional view showing a structure of a semiconductor device immediately after forming the conductive layer in Example 1.

Fig. 2 is a cross sectional view showing a structure upon completion up as far as the mask forming step in Example 1.

Fig. 3 is a cross sectional view showing a structure after removing a region of a conductive layer in Example 1 not covered with a photo-mask (non-masked region) by means of dryetching.

Fig. 4 is a cross sectional view showing a structure after removing masking resist by ashing followed by cleaning with a organic solvent after dryetching in Example 1.

Fig. 5 is a cross sectional view showing a structure after cleaning the semiconductor device shown in Fig. 4 by using the cleaning agent for the semiconductor device according to the present invention in Example 1.

Fig. 6 is a cross sectional view showing a structure of a semiconductor device immediately after forming the conductive layer in Example 4.

Fig. 7 is a cross sectional view showing a structure upon completing up as far as the mask forming step in Example 4.

Fig. 8 is a cross sectional view showing a structure after removing a region of a conductive layer in Example 4 not covered with a photo-mask (non-masked region) by means of dryetching.

Fig. 9 is a cross sectional view showing a structure after removing a masking resist by ashing followed by cleaning with an organic solvent after dryetching in Example 4.

Fig. 10 is a cross sectional view showing a structure after cleaning the semiconductor device shown in Fig. 9 by using the cleaning agent for the semiconductor device according to the present invention in Example 4.

- 1 CVD oxide layer
- 2 TiW layer
- 3 CVD-W layer
- 4 Al-Si-Cu layer
- 5 TiN layer
- 6 PLASMA TEOS layer
- 7 photoresist
- 8 side wall protecting deposition film
- 9 CVD oxide layer
- 10 Ti layer
- 11 TiN layer
- 12 W (tungsten) layer
- 13 photoresist
- 14 side wall protecting deposition film

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

The quaternary ammonium salt used in the present invention is represented by the following formula:



in which R represents an alkyl group of 1 to 4 carbon atoms or a hydroxyl substituted alkyl group of 1 to 4 carbon atoms,  $R_1$  represents an alkyl group of 1 to 4 carbon atoms and X represents an organic or inorganic acid group.

Examples of the quaternary ammonium salt represented by the foregoing general formula include tetramethylammonium formate, tetramethylammonium acetate, tetramethylammonium propionate, tetramethylammonium butyrate, tetramethylammonium oxalate, tetramethylammonium malonate, tetramethylammonium maleate, tetramethylammonium fumarate, tetramethylammonium citraconate, tetramethylammonium benzoate, tetramethylammonium toluate, tetramethylammonium phthalate, tetramethylammonium acrylate, trimethyl(2-hydroxyethyl)-ammonium formate, trimethyl(2-hydroxyethyl)-ammonium acetate, trimethyl(2-hydroxyethyl)-ammonium benzoate, trimethyl(2-hydroxyethyl)-ammonium phthalate, tetraethylammonium formate,

tetraethylammonium acetate, tetrapropylammonium formate, tetrapropylammonium acetate, tetrabutylammonium formate, tetrabutylammonium acetate, tetramethylammonium borate, tetramethylammonium phosphate, tetramethylammonium sulfate, trimethyl(2-hydroxyethyl)-ammonium borate, trimethyl(2-hydroxyethyl)-ammonium phosphate and trimethyl(2-hydroxyethyl)ammonium sulfate.

The concentration of the quaternary ammonium salt in the cleaning agent for the semiconductor device according to the present invention is within a range from 1 to 60%, preferably, 10 to 50% by weight. If the concentration of the quaternary ammonium salt is less than 1% by weight, violent corrosion undesirably occurs to the wiring material, whereas if it is more than 60% by weight, the removing rate for the side wall protecting deposition film is unfavorably lowered.

As the fluoro-compound in the cleaning agent for the semiconductor device according to the present invention there are mentioned, for example, hydrofluoric acid, ammonium fluoride, ammonium hydrogen fluoride, ammonium borofluoride, tetramethylammonium fluoride and tetramethylammonium hydrogen fluoride.

The concentration of the fluoro-compound is from 0.1 to 10, preferably, 0.5 to 5% by weight. If the concentration of the fluoro-compound is less than 0.1% by weight, the removing rate for the side wall protecting deposition film is lowered, whereas violent corrosion occurs to the wiring material at a concentration higher than 10% by weight.

As the organic solvent to be further added in the present invention, there are mentioned an amide such as dimethylformamide, dimethylacetamide, formamide and N-methylpyrrolidone, a lactone such as  $\gamma$ -butyrolactone, a nitrile such as acetonitrile and benzonitrile, an alcohol such as methanol, ethanol, isopropanol and ethylene glycol and an ester such as methyl acetate, ethyl acetate and methyl benzoate.

The concentration of the organic solvent is from 1 to 60%, preferably, 20 to 55% by weight. If the concentration of the organic solvent is less than 1% by weight, violent corrosion occurs to the wiring material, whereas the removing rate for the side wall protecting deposition film is lowered at a concentration higher than 60% by weight.

The temperature of the cleaning agent for the semiconductor device according to the present invention upon removing the side wall protecting deposition film is usually ordinary temperature, for example, 18 to 25°C. If the removing rate for the side wall protecting deposition film is remarkably low, it is used being heated, for example, to 25 to 60°C. Further, the cleaning temperature and the cleaning time are properly selected considering the

state of the side wall protecting deposition film and the kind of the wiring materials.

Upon peeling of the side wall protecting deposition film by cleaning, the peeling step is put into practice by applying the cleaning agent according to the present invention to a conventional method in which the semiconductor substrate to be processed is subjected, for example, to dipping cleaning by batch-wise system or to spray cleaning for each substrate, followed by cleaning with purified water and drying to complete the objective peeling process.

The cleaning agent for the semiconductor device according to the present invention is used in the process for manufacturing the semiconductor device for the purpose of removing a protecting deposition film formed on the side walls of the conductive layer and the photoresist when a wiring structure by dryetching is formed after forming a mask with the photoresist for the conductive layer formed on the semiconductor substrate with a positive or negative type single-layer photoresist or a multilayer photoresist. Since the protecting deposition film can be peeled highly reliably by using the above-mentioned cleaning agent, the surface of the conductive layer is decontaminated and cleaned, so that no corrosion occurs.

Further, the cleaning agent for the semiconductor device according to the present invention is applicable also to the removal of the protecting deposition film formed upon dryetching of a titanium or tungsten layer which has heretofore been difficult to remove and thus making itself effectively usable in the manufacture of a semiconductor device or highly integrated circuit of a multilayer structure.

In addition, mention will be made of the following advantages in using the cleaning agent for the semiconductor device according to the present invention.

- (1) Protecting deposition film formed on the side walls of the conductive film and the photoresist which has heretofore been difficult to remove can certainly be peeled in a short period of time at about ordinary temperature.
- (2) An aluminum alloy or the like as a wiring material does not undergo etching in using the present cleaning agent.
- (3) Since water is usable for rinsing after using the present cleaning agent, the rinsing operation is extremely facilitated.

In the following, the present invention will now be explained more specifically with reference to non-limitative examples along with comparative Examples.

#### Example 1

When a mask was formed with a photoresist to a semiconductor device immediately after forming a conductive layer of a structure shown in Fig. 1 and a wiring structure was formed by dryetching, a side wall protecting deposition film formed on the side walls of the conductive layer and the photoresist was cleaned.

In the semiconductor device immediately after forming a conductive layer shown in Fig. 1, there were successively formed, on a CVD oxide layer 1 as an intermediate insulation film, a TiW layer 2 as a first metal film layer; a CVD-W layer 3 as a second metal film layer; an Al-Si-Cu layer 4 as a third metal film layer; a TiN layer 5 as anti-reflection film; and a PLASMA TEOS layer 6 as a chemical resistant protecting film. Each of the metal films has a thickness of 600Å for the first metal film layer 2, 500Å for the second metal film layer 3, 5000Å for the third metal film layer, 200Å for the TiN layer 5 as the upper film layer and 400Å for the PLASMA TEOS film 6. The Al-Si-Cu layer 4 contained 1% by wt% of Si and 0.5% by weight of Cu.

Fig. 2 shows a structure upon completion up as far as a mask forming process. A positive type photoresist 7 was applied to the conductive layer shown in Fig. 1 and then exposed to form a resist mask portion. The photoresist 7 used therein had a multilayer resist composed mainly of a novolac resin.

Fig. 3 shows a structure after removing a region of the conductive layer not covered with the photo-mask (nonmasked region) by means of dryetching using a chloro-gas. Formation of the side wall protecting deposition film 8 was already observed on the side of the patterned conductive layer.

Fig. 4 shows a structure after removing the masking resist by ashing followed by cleaning with an organic solvent after dryetching. It was confirmed that removal of the side wall protecting deposition film 8 was difficult by this method.

Fig. 5 shows the structure after cleaning the semiconductor device shown in Fig. 4 by using a cleaning agent for the semiconductor device according to the present invention. A solution of ammonium fluoride/tetramethylammonium formate/dimethylformamide/water at 1/10/40/49(wt% ratio) was used as the cleaning agent for the semiconductor device and cleaning was carried out at 23°C for 20 min, followed by water washing.

It can be seen from Fig. 5 that the side wall protecting deposition film 8 in Fig. 4 is completely removed by using the cleaning agent for the semiconductor device according to the present invention, so that the surface of the patterned conductive

layer is decontaminated and cleaned.

#### Example 2

The same semiconductor device as that in Fig. 4 for Example 1 was cleaned by using a cleaning solution having a composition consisting of ammonium fluoride/tetramethylammonium formate/water at 2/45/53 (wt% ratio) at 23 °C for 20 min and then washed with water. As a result, the side wall protecting deposition film was completely removed in the same manner as in Example 1, so that the surface of the patterned conductive layer was decontaminated and cleaned.

#### Example 3

The same semiconductor device as that in Fig. 4 for Example 1 was cleaned by using a cleaning solution having a composition consisting of tetramethylammonium fluoride/tetramethylammonium acetate/dimethylacetamide/water at 5/15/40/40 (wt% ratio) at 25 °C for 30 min and then washed with water. As a result, the side wall protecting deposition film was completely removed in same manner as in Example 1, so that the surface of the patterned conductive layer was decontaminated and cleaned.

#### Comparative Example 1

The same semiconductor device as that in Fig. 4 for Example 1 was cleaned by using a commercially available cleaning solution (alkaline resist cleaning solution) at 100 °C for 10 min as the cleaning conditions. As a result, the side wall protecting deposition film could not be removed.

#### Comparative Example 2

The same semiconductor device as that in Fig. 4 for Example 1 was cleaned by using a 1% by weight aqueous solution of ammonium fluoride at 23 °C for 20 min. As a result, it was observed that although the side wall protecting deposition film could be removed, violent corrosion resulted in the Al-Si-Cu layer.

#### Example 4

When a mask was formed with a photoresist to a semiconductor device immediately after forming a conductive layer of a structure shown in Fig. 6 and wiring structure was formed by dryetching, side wall protecting deposition film formed on the side walls of the conductive layer and the photoresist was cleaned.

In the semiconductor device immediately after forming the conductive layer in Fig. 6, there were successively formed, on a CVD oxide film 9 as an intermediate insulation film, a Ti layer 10 as a first metal film layer; a TiN layer 11 as a second metal film layer; and a W (tungsten) layer 12 as a third metal film layer.

The film thickness for each of the metal films was 300 to 500 Å for the first metal film layer 10, 500 to 700 Å for the second metal film layer 11 and 3000 Å for the third metal film layer 12.

Fig. 7 shows a structure upon completion up as far as mask forming step. A positive type photoresist 13 was applied to the conductive layer shown in Fig. 6 and then exposed to form a resist mask portion. The photoresist 13 used therein had a multilayer resist composed mainly of a novolac resin.

Fig. 8 shows a structure after removing a region of the conductive layer not covered with the photo-mask (nonmasked region) by means of dryetching. Formation of the side wall protecting deposition film 14 was already observed on the side of the patterned conductive layer.

Fig. 9 shows the structure after removing the masking resist by ashing, after dryetching. It was confirmed that although the removal was possible up as far as the resist but the removal of the side wall protecting deposition film 14 was difficult by this method.

Fig. 10 shows a structure after cleaning the semiconductor device in Fig. 9 by using a cleaning agent for the semiconductor device according to the present invention. An aqueous solution of ammonium fluoride/tetramethylammonium formate/dimethylformamide/water at 1/10/40/49 (wt% ratio) was used as the cleaning agent for the semiconductor device and cleaning was carried out at 23 °C for 20 min, followed by water washing and drying. It can be seen in Fig. 10 that the side wall protecting deposition film 14 is removed and the surface of the patterned conductive layer is decontaminated and cleaned.

#### Example 5

The same semiconductor device as that in Fig. 9 for Example 4 was cleaned by using a cleaning solution having a composition consisting of ammonium fluoride/tetramethylammonium formate/water at 2/45/53 (wt% ratio) at 23 °C for 20 min and then washed with water. As a result, the side wall protecting deposition film 14 was completely removed in same manner as in Example 4, so that the surface of the patterned conductive layer was decontaminated and cleaned.

**Example 6**

The same semiconductor device as that in Fig. 9 for Example 4 was cleaned by using a cleaning solution having a composition consisting of ammonium fluoride/trimethyl(2-hydroxyethyl)ammonium formate/dimethylformamide/water at 2/20/30/48 (wt% ratio) at 25 °C for 20 min and then washed with water. As a result, the side wall protecting deposition film 14 was completely removed in same manner as in Example 4, so that the surface of the patterned conductive layer was decontaminated and cleaned.

**Comparative Example 3**

The same semiconductor device as that in Fig. 9 for Example 4 was cleaned by using a commercially available cleaning solution (alkaline resist cleaning solution) at 100 °C for 20 min as the cleaning conditions. As a result, the side wall protecting deposition film 14 could not be removed.

**Comparative Example 4**

The same semiconductor device as that in Fig. 9 for Example 4 was cleaned by using a cleaning solution having a composition consisting of tetramethylammonium formate/dimethylformamide/water at 10/40/50 (wt% ratio) at 25 °C for 30 min as the cleaning conditions, followed by water washing. As a result, the side wall protecting deposition film 14 could not be removed.

**Claims**

1. A cleaning agent for a semiconductor device which comprises a quaternary ammonium salt represented by the general formula:



in which R represents an alkyl group of 1 to 4 carbon atoms or a hydroxyl-substituted alkyl group of 1 to 4 carbon atoms, R<sub>1</sub> represents an alkyl group of 1 to 4 carbon atoms and X represents an organic or inorganic acid group; and a fluoro-compound.

2. The cleaning agent according to Claim 1 which further comprises 1 to 50% by weight of at least one organic solvent selected from the group consisting of amides, lactones, nitriles, alcohols and esters.
3. The cleaning agent according to Claim 1 wherein the concentration of said quaternary ammonium salt in said cleaning agent is within

a range of 1 to 60% by weight.

4. The cleaning agent according to Claim 2 wherein the concentration of said quaternary ammonium salt in said cleaning agent is within a range of 1 to 60% by weight.
5. The cleaning agent according to Claim 1 wherein said fluoro-compound is at least one compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium hydrogen fluoride, ammonium borofluoride, tetramethylammonium fluoride and tetramethylammonium hydrogen fluoride.
6. The cleaning agent according to Claim 2 wherein said fluoro-compound is at least one compound selected from the group consisting of hydrofluoric acid, ammonium fluoride, ammonium hydrogen fluoride, ammonium borofluoride, tetramethylammonium fluoride and tetramethylammonium hydrogen fluoride.
7. The cleaning agent according to Claim 1 wherein the concentration of said fluoro-compound in said cleaning agent is within a range of 0.1 to 10% by weight.
8. The cleaning agent according to Claim 2 wherein the concentration of said fluoro-compound in said cleaning agent is within a range of 0.1 to 10% by weight.
9. The cleaning agent according to Claim 2 wherein the amide is selected from dimethylformamide, dimethylacetamide, formamide and N-methylpyrrolidone; the lactone is selected from  $\gamma$ -butyrolactone; the nitrile is selected from acetonitrile and benzonitrile; the alcohol is selected from methanol, ethanol, isopropanol and ethylene glycol; and the ester is selected from methyl acetate, ethyl acetate and methyl benzoate.
10. The cleaning agent according to Claim 2 wherein the concentration of said organic solvent in said cleaning agent is within a range of 1 to 60% by weight.
11. A method of manufacturing a semiconductor device by forming a mask with a photoresist on a conductive layer formed on a semiconductor substrate and containing at least one of titanium, tungsten, aluminum and aluminum alloy and then forming a wiring structure by dryetching which method comprises a cleaning step of peeling a protecting deposition film formed on side walls of the conductive layer

and the photoresist by using a cleaning agent for a semiconductor device comprising a quaternary ammonium salt represented by the general formula:



in which R represents an alkyl group of 1 to 4 carbon atoms or a hydroxyl substituted alkyl group of 1 to 4 carbon atoms, R<sup>1</sup> represents an alkyl group of 1 to 4 carbon atoms and X represents an organic or inorganic acid group; and a fluoro-compound.

12. The method according to Claim 11 wherein the cleaning agent further comprises 1 to 50% by weight of at least one organic solvent selected from the group consisting of amides, lactones, nitriles, alcohols and esters.

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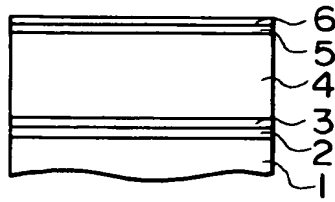


FIG. 1

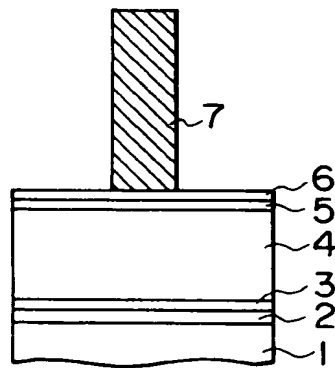


FIG. 2

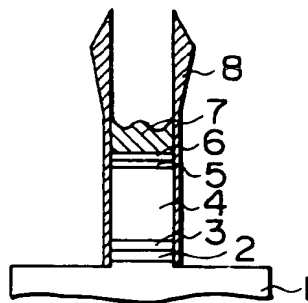


FIG. 3

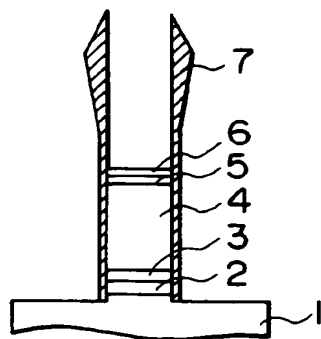


FIG. 4

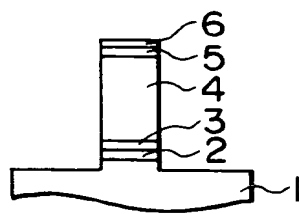


FIG. 5

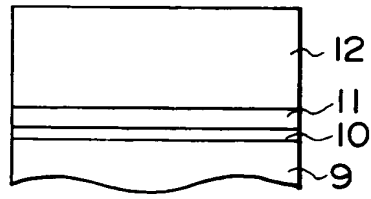


FIG. 6

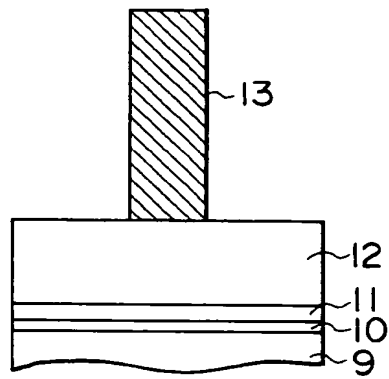


FIG. 7

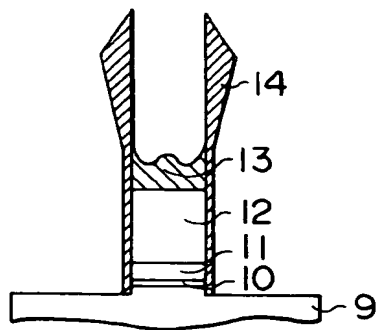


FIG. 8

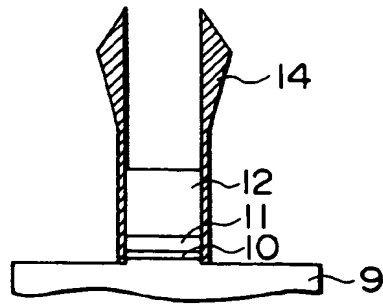


FIG. 9

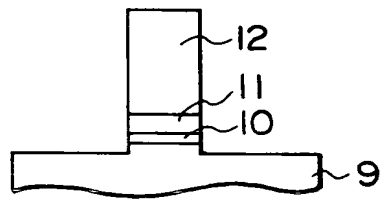


FIG. 10